ENVIRONMENTAL PROTECTION

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DIMINISHING ATMOSPHERIC POLLUTION IN PRODUCTION OF POLISHED GLASS

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A block diagram and a short description of the process of production of sheet glass by the floating ribbon method (float process) are presented. A method for reducing toxic emissions into the atmosphere is described.

The production of sheet and especially polished glass in the glass industry of Russia has been improved by means of intensification, mechanization, and introduction of automatic control of the process, widening the range of products and improving their quality. Some plants have been equipped with highly-automated proportioning and mixing shops with a transfer line for receiving the raw materials, proportioning the components, mixing, and transporting them to the glass melting furnaces. The operations of preparing the batch are conducted in an automated regime. This creates requirements for using optimum batch compositions that provide highgrade glass and promote a decrease in harmful emissions into the atmosphere.

In recent years much attention has been paid to the use of production processes that make it possible to reduce toxic emissions. This first concerns production by the float method, characterized by high output of the glass furnaces and good quality of the products. The first float line in Russia (Figs. 1 and 2) was installed in the Borskii glass plant over 25 years ago and is still operating quite successfully.

The liquid glass from the melting part of the bath furnace passes through a shallow and narrow channel and an inclined overflow chute into a float bath (Fig. 3) with molten tin, where it is shaped into a ribbon and cooled to the temperature at which it arrives at the annealing furnace. The overflow channel is equipped with stopping and regulating doors. The latter door serves for changing the amount of molten glass fed into the float bath and separating the gas media of the float bath and the bath furnace.

The temperature of the liquid glass before the stopping door in the overflow channel is measured by a thermocouple immersed into it to a depth of 20-25 mm and attains 1080°C. The temperature of the liquid glass is sustained automatically by blowing cold air into the cooling part of the furnace. As the liquid glass moves over it, the temperature decreases; in the excape chute it is 1050°C, in the beginning of the zone of spreading over the tin melt it is about 1000°C, and in the end of this zone it is about 950°C.

The float bath contains about 120 tons of molten tin. The depth of the layer of the melt is 40-100 mm. The length of the bath is 46-61 m, the width in the front part is 6600-7200 mm, and in the rest of the bath it is 4000-4500 mm.

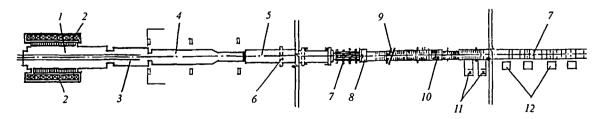


Fig. 1. Line for production of polished glass: 1) melting part of bath furnace; 2) regenerators; 3) cooling part of bath furnace; 4) float bath; 5) annealing furnace; 6) bay for air cooling of the glass ribbon; 7) roller conveyor; 8) cabin for inspecting the glass quality; 9) beams for cross cutting of the glass; 10) accelerating roller conveyor; 11) six cutting tables; 12) tables for cutting small pieces.

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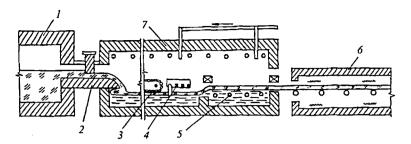


Fig. 2. Diagram of two-stage shaping of a glass ribbon on the surface of molten tin: 1) glass melting furnace; 2) overflow channel; 3) spread-limiting mechanism; 4) electromagnetic inductors; 5) coolers; 6) annealing furnace; 7) molten pool.

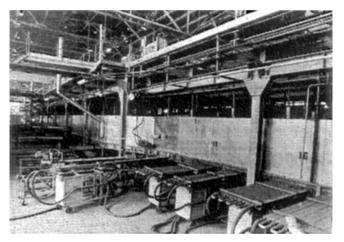


Fig. 3. Float bath with suspended coolers for cooling the glass ribbon.



Fig. 4. Panel for controlling the float process.

Electric heaters are mounted under the roof over the entire length of the bath and provide the requisite temperature over the entire surface. The bottom is cooled by air flow. The operations of transferring the ribbon during the start of the installation are conducted manually through the side windows of the float bath.

An inert gas consisting of nitrogen mixed with hydrogen (at most 0.0001% oxygen is permissible) is fed into the bath

continuously under excess pressure. The inert gas protects the tin from oxidation and eliminates the formation of an oxide film on the lower surface of the glass ribbon. The gas is removed through low-density sites in the lining and the site of passage of the ribbon into the annealing furnace.

The tin melt contains oxygen and sulfur impurities. In order to remove, them the melt is enriched with 0.005% sodium or 0.001% magnesium which reacts with oxygen and sulfur, forming a slag withdrawn mechanically or by regenerating the tin. Another source of slag is diffusion of Na₂O from the glass into the molten tin and con-

densation of the products of the reaction between tin and oxygen in the cold end of the bath. Figure 4 shows the panel for controlling the float process.

Practice has shown that the equilibrium thickness of the liquid glass layer when it spreads over the tin melt is about 6 mm. At a lower thickness, the spreading rate decreases markedly under the action of the force of gravity of the liquid glass. The rate of the process in the zone of spreading of the liquid glass over the tin melt increases with the temperature and decreases considerably with a reduction in the thickness of the glass layer. In order to obtain a ribbon 3 mm thick (or thinner), it is subjected to forced stretching.

At the beginning of the bath, the liquid glass layer is 20-25 mm thick and as it spreads, passing from the wide part of the bath into the narrow one, the layer attains the equilibrium thickness at a temperature of $920-950^{\circ}$ C. Graphite stoppers prevent contact between the shaped glass ribbon and the walls of the bath. After they are passed, the width and thickness of the ribbon are fixed completely. As the ribbon is transferred to the outlet, it cools to 600° C and enters the roller conveyor of the annealing furnace.

As the liquid glass is refined during the melting process in the bath furnace, gaseous products are emitted from the melt. The maximum temperature in the refining zone is $1560-1600^{\circ}\text{C}$. By the end of the refinement stage the liquid glass is free of visible gas inclusions, though in the beginning of the process it contains a considerable amount of gases in a dissolved state or in the form of bubbles of various sizes. The gaseous substances are mainly the products of decomposition of the batch components, i.e., carbonates, sodium sulfate, and coal. These are SO_2 , SO_3 , CO_2 , and partially CO. A certain amount of oxygen and nitrogen can be present.

One volume fraction of liquid glass contains up to five volume fractions of dissolved gases on average. Since this proportion at the temperature of glass refining considerably exceeds the equilibrium state of the system, the gases are removed from the melt by diffusing to its surface and then into the furnace atmosphere. This is accompanied by diffusion of the gases to the external surfaces of the bubbles contained in the liquid glass and then inside the bubbles, which increases their volume and promotes their floating up and removal into the furnace atmosphere. The formation and growth of new bubbles occurs simultaneously. The introduction of refining

impurities accelerates growth and floating of bubbles to the surface of the liquid glass and causes a decrease in the partial pressure of the gases contained in it.

The producers were faced with the problem of reducing emission of harmful components, and especially SO₃, into the atmosphere.

The plant produces polished glass of the following composition (in mass fractions): 73.0% SiO₂, 0.9% Al₂O₃, 0.1% Fe₂O₃, 8.7% CaO, 3.6% MgO, 13.4% Na₂O, and 0.3% SiO₃. The composition of the corresponding batch is presented in Table 1.

The daily discharge of liquid glass from two furnaces with utilization factor equal to 0.75 and a mean yearly output of about 24 mln m² of glass products of various thicknesses amounts to 900 – 950 tons. Every hour the two production lines (LPS-1 and LPS-2) used to emit 62 m³ sulfuric anhydride, polluting the ambient.

In 1996 a group of workers¹ suggested changing the composition of the batch (see Table 1) by decreasing the content of sodium sulfate and coal by a factor of 1.5-2. This did not change the specified composition of the glass and the quality of the product.

The ratio of alkalis introduced into the glass with soda and sodium sulfate was changed from the traditional 96-to-4% to 97.15-to-2.8.5%. The

content of sodium sulfate in the batch decreased from 1.00 to 0.71% at a moisture content of 4.5%. Sodium sulfate contains 43.7% Na₂O and 56.3% SO₃. The latter component formed in the process of glass melting in a high amount is especially toxic for the environment. At the same time, the introduction of sodium sulfate into the batch is necessary; it activates the refining process, accelerates growth of the number and size of bubbles formed in melting, and decreases the surface tension of the liquid glass surrounding the bubbles. Coal added to the charge during the melting process accelerates decomposition of the sodium sulfate. Therefore, the content of both components (sodium sulfate and coal) in the new composition of the batch was decreased simultaneously. Calculations showed that the redox potential of the reactions that occur in melting of traditional and new batches under the conditions of the plant did not change.

TABLE 1

Batch components	Conventional composition		New composition		Standard consumption per 1 ton batch, kg	
	%	per 1 weighed portion, kg	%	per 1 weighed portion, kg	conventional composition	new composition
Sand	58.80	1140.0	59.26	1165.0	591.0	595.6
Feldspar	2.66	51.8	2.68	52.2	26.9	27.1
Soda	17.88	343.5	18.15	353.8	179.5	182.2
Sodium sulfate	0.99	19.4	0.71	13.8	10.0	7.2
Lime	4.30	83.3	5.20	101.4	48.1	58.1
Dolomite	15.27	297.6	13.95	271.9	171.0	156.2
Coal	0.10	2.0	0.05	1.0	1.03	0.53

TABLE 2

Batch	Cost of	Conventional as calculate	•	New composition as calculated per 1 ton	
composition	I ton, rub	standard con- sumption, kg	cost or raw material, rub	standard con- sumption, kg	cost or raw material, rub.
Sand from Ramen-					
skoe deposit	144,000	591.0	85,104	595.2	85,709
Feldspar	348,070	26.9	9363	27.0	9398
Soda ash	945,300	179.5	169,681	182.2	172,234
Sodium sulfate	713,500	10.0	7135	7.2	5137
Lime	74,000	48.1	3559	58.1	4299
Dolomite	78,400	171.0	13,406	154.0	12,074
Milled coal	3,640,000	1.03	3749	0.53	1929

The yield of sulfuric anhydride from sodium sulfate is 0.0054 kg per 1 kg batch and its volume is 0.0019 m³ per 1 kg batch. LPS-1 and LPS-2 lines consume 31 900 kg/h of batch, emitting 62 m³/h SO₃ in the case of the conventional composition and 43.4 m³/h in the case of the new one. The emission of sulfuric anhydride into the atmosphere decreased by 18.6 m³/h or 30% of the initial volume. The total reduction in emissions of SO₃ into the atmosphere during a year amounts to 162,900 m³ or 402,000 m³, where the temperature of the emitted gas is equal to 450°C.

In addition to improving the ecological situation, the use of the new batch composition has a certain economic effect. It can be seen from Table 2 that the reduction in the content of sodium sulfate and coal in the composition of the batch decreases the cost of 1 ton of batch from 291,997 thousand rubles to 290,780 thousand rubles. At an annual consumption of 222,794 tons of batch, the economic effect of the use of the new composition exceeds 270 mln rubles in 1996 prices.

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